

## PATENT ABSTRACTS OF JAPAN

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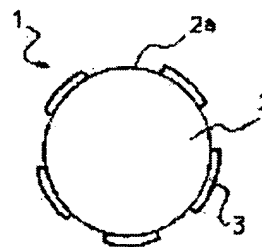
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## (54) PHOTOCATALYTIC PARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photocatalytic particle excellent in photocatalytic property, particularly photocatalytic property in a visible light region.

SOLUTION: The photocatalytic particle is provided with a titanium oxide particle 2 and an organic high molecular semiconductor 3 covering the surface of the titanium oxide particle 2 so as to expose a part of the surface 2a of the titanium oxide particle 2 and the particle diameter of the titanium oxide particle 2 is controlled to  $\leq 1 \mu\text{m}$ . Being irradiated with the visible light or a light having more shorter wave length, the organic high molecular semiconductor covering the titanium oxide particle is excited to generate electrons and positive holes. And because the high molecular semiconductor covers the titanium oxide particle 2 so as to expose a part of the surface of the titanium oxide, the electrons and the positive holes in the covered part are in a movable state between the organic high molecular semiconductor and the titanium oxide. Further, because the titanium oxide of the base material is a fine particle of  $\leq 1 \mu\text{m}$ , quantum size effect is generated.



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CLAIMS

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[Claim(s)]

[Claim 1] a titanium oxide particle and; -- the organic polymeric semiconductor which covers the front face of said titanium oxide particle so that a part of front face of said titanium oxide particle may be exposed -- having --; --; light catalytic particle characterized by the particle size of said titanium oxide particle being 1 micrometer or less.

[Claim 2] Said organic polymeric semiconductor is a light catalytic particle according to claim 1 characterized by being covered by the front face of said titanium oxide particle in the shape of an island.

[Claim 3] Said organic polymeric semiconductor is a light catalytic particle according to claim 1 or 2 characterized by being at least one sort of compounds chosen from a poly para-phenylene compound, the poly thiophene compound, the poly aniline compound, and a phthalocyanine compound.

[Claim 4] The light catalytic particle according to claim 1 to 3 to which the weight ratio to said light catalytic particle of said covered organic semiconductive polymer is characterized by being 10 - 40%.

[Claim 5] The light catalytic particle according to claim 1 to 4 characterized by covering said organic semiconductive polymer with physical vapor deposition.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is used for disassembly of dirt, such as decomposition of the oil which adhered to the cooking appliance etc. especially, and a sheathing material, deodorization, immobilization of a carbon dioxide, etc. about the light catalytic particle which has a photocatalyst operation, and relates to a suitable light catalytic particle.

[0002]

[Description of the Prior Art] Conventionally, using gamma-manganese oxide as a catalyst, the approach (heat catalyst) of heating an oil together with this and promoting the perfect combustion of an oil and titanium oxide were applied to support, such as a steel plate and a filter, and the approach by the photocatalyst which decomposes oil has been used for disassembly of an oil by irradiating ultraviolet rays at this. Since especially a photocatalyst does not need to hold an object to an elevated temperature on the occasion of decomposition like a heat catalyst, need is increasing quickly in recent years. Moreover, it was also known that what carried out the ion implantation of the transition metals, such as Cr, to titanium oxide has a photocatalyst operation in a light region.

[0003]

[Problem(s) to be Solved by the Invention] However, in use, the ultraviolet ray lamp was needed and the inorganic system photocatalyst represented by the above titanium oxide also had to take the optical cutoff to the body into consideration, in order that a catalysis might not break out, if it was not ultraviolet rays. Moreover, the photocatalyst using an ion implantation had the high manufacturing cost, and it was difficult to use it for a large area practically.

[0004] Then, this invention aims at offering the light catalytic particle which was excellent in the photocatalyst property and was especially excellent in the photocatalyst property in a light field.

[0005]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as shown in drawing 1, the light catalytic particle 1 by invention concerning claim 1 is equipped with the organic polymeric semiconductor 3 which covers the front face of the titanium oxide particle 2 so that a part of surface 2a of the titanium oxide particle 2 and; titanium oxide particle 2 may be exposed, and is characterized by the particle size of; titanium oxide particle 2 being 1 micrometer or less.

[0006] Thus, if constituted, since an organic semiconductive polymer will be covered, if the light of wavelength shorter than a light region or it is irradiated by the organic semiconductive polymer, it will be excited and an electron and an electron hole will be produced.

Moreover, since an organic polymeric semiconductor is covered so that a part of front face of titanium oxide may be exposed, in the covered part, it is in the condition which can move in an electron or an electron hole between an organic polymeric semiconductor and titanium oxide. Furthermore, since the titanium oxide which is a base material is a particle 1 micrometer or less, a quantum size effect can be produced.

[0007] Moreover, it is [ like ] desirable that according to claim 2 the organic polymeric semiconductor 3 is covered with the light catalytic particle 1 according to claim 1 by the front face of the titanium oxide particle 2 in the shape of an island.

[0008] Thus, if constituted, since the particle size of the titanium oxide which is a base material is 1 micrometer or less and the organic semiconductive polymer is covered by it in the shape of an island, these electrons and electron holes become a reactant high thing according to the quantum size effect of an organic semiconductive polymer, without receiving thermal relaxation with a grid. A part of electron emitted here and electron hole are supplied to the titanium oxide which is a base material, it is multiplied by the electron and electron hole which it is excited by the ultraviolet rays slightly included in the light on the surface of titanium oxide, and are generated, and promotes the photocatalyst activity of titanium oxide.

[0009] Furthermore, it is desirable to consider as at least one sort according to claim 3 as which the organic polymeric semiconductor 3 is chosen from a poly para-phenylene compound, the poly thiophene compound, the poly aniline compound, and a phthalocyanine compound like by the light catalytic particle 1 according to claim 1 or 2 of compounds.

[0010] Especially a phthalocyanine compound is a compound which can be used also as an organic pigment, and is easy to come to hand.

[0011] Moreover, it is desirable that the weight ratio to the light catalytic particle 1 of the organic semiconductive polymer 3 according to claim 4 covered with the light catalytic particle 1 according to claim 1 to 3 like is 10 - 40%.

[0012] Since the coverage of an organic semiconductive polymer is in 10 - 40% of the weight of the range at this time, island-like covering of an organic semiconductive polymer is attained, and supply of enough electrons for titanium oxide and an electron hole is performed.

[0013] Furthermore, physical vapor deposition may cover the organic semiconductive polymer 3 by the light catalytic particle according to claim 1 to 4 like a publication to claim 5.

[0014] In this case, since an organic semiconductive polymer is covered with physical vapor deposition, the organic substance is firmly covered in the shape of an island on a particle, and is joined firmly electrically.

[0015]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. Drawing 1 is the extension mimetic diagram having taken out and shown the light catalytic particle by this invention only one piece. The organic semiconductive polymer 3 is covered so that the part may be exposed to surface 2a of the titanium oxide 2 which is the base material which carried out the globular form mostly among drawing.

[0016] Here, it has the photocatalyst operation, as for these, a macromolecule chain forms conjugated double bond, and not only mineral matter like titanium oxide but the organic substance is characterized by a band gap being comparatively wide. A typical thing is a poly paraphenylene compound (derivative) among such things. Unlike an inorganic photocatalyst, such an organic photocatalyst demonstrates a catalysis with the light of the comparison-long wavelength near a light field. However, such photocatalyst effectiveness is not so strong as it can disassemble an oil and dirt. Although this invention has the strong photocatalyst effectiveness for such the organic substance, it uses the synergistic effect by combining with the titanium oxide which needs ultraviolet rays.

[0017] In drawing 1, the magnitude of the titanium oxide particle 2 of a base material is 1 micrometer or less. This may be 0.5 micrometers or less desirably [ it is required in order to raise the electron at the time of the organic semiconductive polymer 3 covered to surface 2a exciting, and the reactivity of an electron hole, and ]. If the magnitude of the titanium oxide particle 2 of a base material exceeds 1 micrometer, the electron and electron hole which the organic semiconductive polymer 3 by which surface coating was carried out excites and generates will disappear by lattice vibration, and will stop being able to discover photocatalyst activity easily.

[0018] Here, this organic polymeric semiconductor 3 is covered by the base material titanium oxide particle 2 in the shape of an island. It is because the photocatalyst activity of titanium oxide will not be discovered if covered completely.

[0019] Moreover, in order to receive the above-mentioned electron and supply of an electron hole, titanium oxide 2 and the organic semiconductive polymer 3 must be joined electrically. Therefore, it is both so-called mixture, and when electric junction cannot be desired, effectiveness like this invention is not discovered.

[0020] What is necessary is just to make the amount of covering of the organic semiconductive polymer 3 into 10 - 40% of the weight of the range to the weight of the light catalytic particle 1, in order to attain such island-like covering and to perform supply of enough electrons for titanium oxide 2, and an electron hole.

[0021] Moreover, in order to strengthen electric junction, it is desirable to lessen mixing of the impurity in the case of covering as much as possible. Physical vapor depositions which are decompressing among a vacuum as the covering approach and are processed from this point, such as vacuum deposition and sputtering, are desirable.

[0022] Island-like covering means the condition that the organic semiconductive polymer 3 is covered with one or more discontinuous film, to the titanium oxide particle 2, and the coverage (surface area of the area / titanium oxide particle 2 of the part with which the organic semiconductive polymer 3 is covered by the titanium oxide particle 2) is 20 - 50% of range desirably here.

[0023] Moreover, from a viewpoint of the above-mentioned discontinuity film, a covering configuration can take various gestalten, such as the shape of a line besides the shape of an island, and a muscle, and punctiform, that what is necessary is just to have covered the organic polymeric semiconductor 3 so that a part of surface 2a of the titanium oxide particle 2 may be exposed. Furthermore, when the direction of radiation of light takes that it is not isotropic, either into consideration practically, as shown in drawing 1, it is desirable, although the number of discontinuity film should just be one or more to cover the perimeter of the titanium oxide particle 2 by two or more two or more discontinuity film (the case where five islands are formed on the great circle of the titanium oxide particle 2 which carried out the globular form mostly is shown in drawing 1 ).

[0024] It is the description that, as for the organic semiconductive polymer 3 covered here, the macromolecule chain forms conjugated double bond, and poly paraphenylene (PPP), the poly thiophene (PT), the poly pyridine -2, 5-diyl (PPy), the poly aniline, polythiazyl, a phthalocyanine compound, etc. are specifically mentioned. Among this, generally a phthalocyanine compound is easy to come to hand, and covering by vacuum evaporatio no etc. is also easy the compound, and it is suitable. Moreover, it colors by combining with metal ions, such as copper and nickel, and, generally the phthalocyanine compound is used as an organic pigment. The copper phthalocyanine blue which copper combined is one of the typical thing.

[0025] On the other hand, although the titanium oxide 2 covered has the desirable thing of the point of photocatalyst activity to an anatase mold and the configuration is generally mostly made into a globular form, it is not limited to especially a globular form. Moreover, when condensing remarkably, after cracking, it uses.

[0026] As mentioned above, the industrial use of the titanium oxide particle 2 which covered the organic polymeric semiconductor 3 in the shape of an island is very large by the effectiveness of organic substance decomposition, such as an oil in the conventional ultraviolet-rays wavelength region, not only going up, but being able to disassemble an oil and dirt also in the long wavelength light of a light region, and covering to a steel plate or resin.

[0027] Moreover, physical vapor deposition covers an organic polymeric semiconductor with the gestalt of another operation of this invention on the front face of a titanium oxide particle. Physical vapor deposition is vacuum deposition, sputtering, etc. which are decompressing for example, among a vacuum and are processed. If it covers with physical vapor deposition, the organic substance can cover efficiently in the shape of an island. Moreover, electric junction becomes firm and mixing of the impurity at the time of being covering decreases.

[0028] As physical vapor deposition which can be used by this invention, there are some which are indicated by an artificer's etc. application (JP,9-59532,A). In this physical vapor deposition, the vacuum evaporatio no equipment equipped with fine-particles fluidization equipment and resistance heating equipment in the vacuum housing is used. The electrical potential difference and current of resistance heating equipment are determined according to the sublimation temperature of the organic semiconductive polymer to evaporate, and its amount. 200-700 degrees C of the temperature are usually 300-500 degrees C preferably. Vacuum evaporatio no is performed after usually carrying out vacuum suction to 10 to 2 or less Torrs.

[0029] As a resistor of resistance heating equipment, the resistor which consists of a tungsten, molybdenum, iron, stainless steel, carbon, etc. is desirable. Although the configurations of a resistor may be the shape of a plate, and a letter of a block, its method of wrapping and heating an organic semiconductive polymer in it using a reticulated resistor is the most desirable. The opening of a network has desirable about 25-200 micrometers.

[0030] In addition, by warming mixing [ distribute beforehand approaches other than physics-like arrival, for example, the organic substance, in a solvent, after adding a titanium oxide particle and stirring and filtering it to this, put in the organic substance and a titanium oxide particle into the approach of evaporating a solvent, and a sealing reduced pressure container, and ], melting of the organic substance may be carried out and the approach of covering to titanium oxide or the approach which is made to carry out melting of the organic substance, and is vapor-deposited may be adopted.

[0031]

[Example] Various organic semiconductive polymers were covered to the titanium oxide powder of 0.5 micrometers of example 1 mean diameters. To 1g of this powder, 0.1g of salad oil was added, it mixed, this was put into the glass petri dish with a diameter of 7cm, and it

put on the sealing box gently by making this into an exposure object. And light was irradiated over 7 hours from the location which is distant from a petri dish 250mm with the high pressure mercury vapor lamp of 400W.

[0032] In addition, the temperature rise of the exposure object at the time of this exposure was about 120 degrees C. The weight reduction after an exposure estimated the photocatalyst property in connection with an oil solution under these conditions. The result is shown in the table of drawing 2 and drawing 3. In addition, the result of having evaluated only the titanium oxide of the particle size same as comparison material by the same approach is also shown collectively.

[0033] These results show that the light catalytic particle of this example is excellent in an oil solution property only compared with titanium oxide under UV irradiation. Moreover, it also turns out that especially the phthalocyanine compound is excellent from this example. Furthermore, the covering approach is also known by that especially physical vapor deposition is excellent.

[0034] The same evaluation as an example 1 was performed to the same powder as example 2 example 1 using the incandescent lamp of 200W which can irradiate light with the wavelength in the range of the light from infrared radiation. The result is shown in the table of drawing 4 and drawing 5.

[0035] These results show that the light catalytic particle of this example excels the ingredient of only titanium oxide in the oil solution property also in the light of infrared radiation to a light field. Moreover, it also turns out that especially the phthalocyanine compound formed especially with vacuum deposition is excellent.

[0036] The copper phthalocyanine blue which is a kind of a phthalocyanine compound was covered with vacuum deposition 30% of the weight to the titanium oxide particle which has the mean diameter of example 3 versatility. At this time, the oil solution property was investigated by the same evaluation approach as an example 1. The result is shown in drawing 6.

[0037] For the amount of oil decomposition, the particle size of a titanium oxide particle is [ the particle size of a titanium oxide particle / the amount of oil decomposition ] about 35mg to about 6mg in 1.1 micrometers, at drawing 6, by 1 micrometer, the amount of oil decomposition rose gradually, and it amounts to about 75mg in 0.5mg, and it amounts to about 85mg in 0.22 micrometers as there to particle size becomes small. the particle size not more than it -- the amount of oil decomposition -- the time of 0.22 micrometers, and \*\*\*\*\* -- it is maintained highly.

[0038] These results show that the particle size of titanium oxide as shown in drawing 6 as A excels [ field / 1 micrometer or less ] in the oil solution property. Moreover, it also turns out that especially the property especially is excellent in the particle size of 0.5 micrometers or less.

[0039] The copper phthalocyanine blue of various weight %s was covered with vacuum deposition to the titanium oxide particle of 0.3 micrometers of example 4 mean diameters. At this time, the same approach as an example 1 estimated the oil solution property by the difference in the amount of covering. The result is shown in drawing 7.

[0040] In drawing 7, although the amount of covering of the amount of oil decomposition is 15mg at 4%, from there, the amount of oil decomposition rose gradually as the amount of covering became [ many / a covering quantitative ratio is ), as for the amount of oil decomposition, the amount of covering was set to about 45mg at 10%, as for the amount of oil decomposition, the amount of covering was set to about 64mg at about 15%, and, as for the amount of oil decomposition, the amount of covering amounts to about 74mg at 20%. As for the amount of oil decomposition, the amount of covering is maintaining about 74mg at least 30%.

[0041] From there, the amount of oil decomposition falls gradually as a covering quantitative ratio becomes large, and as for the amount of oil decomposition, the amount of covering is falling [ the amount of covering ] even to about 15mg by 50% further by about 44mg at 40%. Even if a covering quantitative ratio becomes large more than it, the amount of oil decomposition seldom changes. Incidentally as for the amount of oil decomposition, it turns out that the amount of covering is about 4.5mg at 70%.

[0042] These results show excelling in the oil solution property in the field whose amount of covering as shown in drawing 7 as B is 10 - 40 % of the weight. Moreover, the amount of covering is known by that especially a property is good at 15 - 30 % of the weight.

[0043] As explained above, the light catalytic particle by this invention begins cookware and a kitchen instrument with self-cleaning nature, the application to sheathing, interior building materials, etc. is possible for it, and contribution of industrialization is very large. Moreover, the light catalytic particle by this invention can be used for various fields, such as disassembly of not only an oil solution but nitrogen oxides, or a sulfur oxide, disassembly of organic substance dirt, antibacterial, and carbon-dioxide immobilization.

[0044]

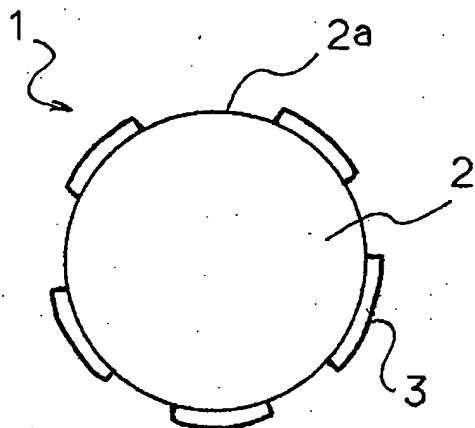
[Effect of the Invention] As mentioned above, according to this invention, since it had the organic polymeric semiconductor which covers the front face of a titanium oxide particle so that a part of front face of a titanium oxide particle may be exposed, and it constituted so that the particle size of a titanium oxide particle might be 1 micrometer or less, the improvement in a property of the titanium oxide as a photocatalyst can be brought about, and the oil solution property in a light field can be raised especially remarkably.

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Drawing selection **Representative drawing** 

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